1-CYANO-1,3-BUTADIENE AND ITS DIELS-ALDER REACTIONS

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GEORGE IRELAND POOS

B.S., Virginia Military Institute, 1947
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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Harold R. Snyder for his very helpful advice and guidance during the course of this study.

The author is also indebted to the University of Illinois for a teaching assistantship from September, 1947, to June, 1948, and for a University Fellowship from September, 1948, to June, 1949. He also wishes to thank the National Research Council for the Atomic Energy Commission Fellowship held since July, 1949. He is also indebted to Miss Elizabeth Petersen and Mrs. Agatha Johnson for the determination and interpretation of the infrared absorption spectra.

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Introduction

Although many different dienes and dienophiles have been employed in the diene synthesis, relatively little work has been reported concerning the determination of the structures of adducts obtained by reactions of unsymmetrical dienes with unsymmetrical dienophiles. It is to be expected that the elucidation of the structures of such products will yield information concerning the factors that control the reaction.

Recent studies of the preparation of 1-cyano-1,3-butadiene have shown that the *cis*- and *trans*-isomers can be separated and that the *trans*-isomer reacts in the Diels-Alder fashion with both butadiene and maleic anhydride (1). Accordingly the *trans*-isomer may be added to the list of unsymmetrical compounds that participate in the diene reaction. The present work was undertaken to determine whether it functions both as a diene and as a dienophile, to determine the structures of some of its Diels-Alder derivatives, to study the behavior of the *cis*-isomer in the Diels-Alder process, and to extend the knowledge of other reactions of the 1-cyano-1,3-butadienes.

Discussion Of Results

Evidence in support of the configurations assigned to the geometric isomers of 1-cyano-1,3-butadiene (1) was obtained by hydrolysis to the corresponding solid amides. Attempts to cyclize 1-cyanobutadiene in the presence of alumina at high temperature resulted in the formation of pyridine in very low yield. Unidentified organic bases and a mixture of isomeric pentenonitriles were also obtained in low yield from the cyclization experiments.

The Diels-Alder adduct of 1-cyano-1,3-butadiene with 1,3-butadiene (1) was shown to be a 2-cyano-1-vinylcyclohexene. Proof of the carbon structure was accomplished by bromina-

tion of the adduct, dehydrobromination and hydrolysis to 2-ethylbenzamide and 2-vinylbenzamide. From a review of the experimental evidence concerning the bond structure of the butadiene adduct, it was apparent that the 2-cyano-1-vinyl-2-cyclohexene structure was most likely. Spectral data, isomerization experiments and addition reactions strongly support this conclusion. Oxidation, halogen addition and attempted reactions with dienophiles also favor the partly conjugated structure. Less conclusive was the evidence obtained from molar refractivity, behavior with the Grignard reagent and hydrolysis. Apparently an equilibrium mixture of amides is obtained by hydrolysis with alkaline hydrogen peroxide. However, the behavior of the butadiene adduct in the hydrogenation experiment was opposite to that to be expected for the partly conjugated structure. This result prohibits an unequivocal assignment of the 2-cyano-1-vinyl-2-cyclohexene structure to the compound.

The cyclic dimer of 1-cyano-1,3-butadiene was isolated and characterized as 1-(β-cyanovinyl)-2-cyano-3-cyclohexene. The structure was proved by aromatization of the dimer to *o*-cyanohydrocinnamonitrile and hydrolysis of this dinitrile to the known *o*-carboxyhydrocinnamic acid (2). Experiments with the *cis*- and *trans*-1-cyanobutadienes showed that the *trans*-isomer is the chief source of the dimer.

Both the *cis*- and *trans*-isomers of 1-cyano-1,3-butadiene were found to give a Diels-Alder product with cyclopentadiene. The adducts were shown to be *cis*- and *trans-endo*-β-(2,5-endomethylene-3-cyclohexenyl)acrylonitrile and thus resulted from the addition of cyclopentadiene as a diene to the terminal olefinic bonds of the cyanobutadienes. Proof of the structures was obtained by alkaline hydrogen peroxide hydrolysis of the compounds to different amides and hydrogenation to the same saturated nitrile. Confirmation of the assignment of structure was obtained by independent synthesis. The condensation of the known *endo*-2,5-endomethylene-3-cyclohexene-1-aldehyde (3) with malonic acid yielded *trans-endo*-β-(2,5-endomethylene-3-cyclohexenyl)acrylic acid. The amide correspond-

ing to this acid was prepared and found to be identical with the *trans*-cyanobutadiene-cyclopentadiene adduct amide.

2,3-Dimethyl-1,3-butadiene and the 1-cyano-1,3-butadiene isomers gave Diels-Alder products analogous to the cyclopentadiene adducts. However, the yields were poorer and the reactions were accompanied by isomerization of the cyanobutadienes. The structures of the 2,3-dimethylbutadiene adducts were shown to be *cis*- and *trans*-β-(3,4-dimethyl-3-cyclohexenyl) acrylonitrile by hydrolysis to different amides and hydrogenation to the same dihydronitrile. The assignment of structure from this information was again confirmed by an independent synthesis of the *trans*-cyanobutadiene adduct amide. Malonic acid and the 2,3-dimethylbutadiene-acrolein Diels-Alder adduct (4) were condensed to give the *trans*-acid from which the corresponding *trans*-β-(3,4-dimethyl-3-cyclohexenyl) acrylamide was prepared for comparison.

The condensation of isoprene with the cyanobutadiene isomers yielded in each case a complex mixture of isomeric adducts. A single nitrile was separated from the reaction products of *cis*-cyanobutadiene and isoprene by fractional distillation and was shown to be *cis*-β-(4-methyl-3-cyclohexenyl) acrylonitrile. Proof of this structure was accomplished by hydrogenation and hydrolysis to β-(4-methyl-3-cyclohexenyl) propionamide which was prepared for comparison by the hydrogenation of *trans*-β-(4-methyl-3-cyclohexenyl) acrylamide. The latter compound was prepared from the corresponding acid which was synthesized by the condensation of malonic acid and the known 4-methyl-3-cyclohexene-1-aldehyde (4).

A single product could not be separated by fractional distillation of the mixture of adducts obtained from isoprene and *trans*-cyanobutadiene. By hydrolysis of various fractions of the partially separated mixture, three isomeric amides were isolated. One of these amides proved to be *trans*-β-(4-methyl-3-cyclohexenyl) acrylamide. Structures were proposed for the two other isomers. It was concluded that isoprene and *trans*-cyanobutadiene function simultaneously as dienes and

dienophiles in the reaction.

Neither the *cis*- nor *trans*-isomer of 1-cyano-1,3-butadiene formed an addition product with anthracene or furan. Since maleic anhydride readily gives adducts with these dienes, it was concluded that cyanobutadiene is less reactive as a dienophile than maleic anhydride.

trans-1-Cyano-1,3-butadiene was found to give single products by Diels-Alder reaction with ethyl acrylate and methyl acrylate. The ethyl acrylate adduct was aromatized by allyl bromination and dehydrobromination to ethyl 2-cyanobenzoate. The structure of the aromatic derivative was proved by hydrolysis to phthalic acid. Hydrolysis of both the ethyl and methyl acrylate adducts of 1-cyano-1,3-butadiene yielded 2-cyclohexene-1,2-dicarboxylic acid which was identified by its melting point and the melting point of its anhydride (5). The acrylate adducts both gave a low yield of *cis*-3-cyclohexene-1,2-dicarboximide when refluxed in the corresponding alcohol with concentrated sulfuric acid. Hydrogenation to the known *cis*-cyclohexane-1,2-dicarboximide (6) was used to establish the structure of the unsaturated imide. The ammonolysis of the known *cis*-4-cyclohexene-1,2-dicarboxylic acid anhydride (3) yielded *cis*-4-cyclohexene-1,2-dicarboximide which was reduced to the known *cis*-cyclohexane-1,2-dicarboximide and used for comparison. The *ortho*- type structure of the acrylic ester adducts of 1-cyanobutadiene is the reverse of that to be expected on the basis of resonance and electronic effects in the reacting molecules. It was concluded that the generally accepted ionic influences were of little importance in this diene reaction.

Acrylonitrile and *trans*-1-cyano-1,3-butadiene gave a low yield of an addition product which could not be isolated in the pure state because of the proximity of its boiling point and that of cyanobutadiene dimer also formed in large proportion in the reaction.

trans-1-Cyano-1,3-butadiene did not give a product with crotonaldehyde, styrene or ethylenesulfonyl chloride. Dimeri-

zation of the cyanodiene appeared to proceed more rapidly than adduct formation with these dienophiles under the conditions of the experiments.

The *cis*-isomer of 1-cyano-1,3-butadiene did not react with ethyl acrylate, methyl acrylate, acrylonitrile, crotonaldehyde, styrene or ethylenesulfonyl chloride. This result was expected in the light of the known non-reaction of the more active dienophile maleic anhydride.

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VITA

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